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DETERMINATION OF THE HEAT OF FUSION OF SILICA

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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DETERMINATION OF THE HEAT OF FUSION OF SILICA

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I. INTRODUCTION.

In carrying out the determination of the heat of fusion of a substance, one has a choice of several different methods and the choice of the best method to be used depends largely upon the physical and chemical properties of the substance and upon its fusion temperature.

For example, in determining the heat of fusion of ice a definite quantity of ice can be allowed to melt in a calorimeter and the amount of heat absorbed measured. This method, however, would not be applicable to a high melting substance, such as quartz. One method, based on the law of Hess, which however can be used in such a case, is to measure the amounts of heat liberated in the reactions of amorphous and crystalline silica with hydrofluoric acid.

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II. DISCUSSION OF PREVIOUS WORK

Mulert* while working on the Thermochemistry of Silicic Acids and Silicates carried out a determination of the heat of fusion of quartz. From 0.5 to 1 gram of silica was allowed to react with 470 cc. of hydrofluoric acid in a calorimeter and the amount of heat liberated, measured. After all the silica had dissolved the excess acid was titrated with carbonate free potassium hydroxide using phenolphthalein as an indicator. The acid used was 20% hydrofluoric acid and the amount used was weighed accurately to 0.01 gram. Silica fine enough to dissolve quickly in the acid could be prepared only by sedimentation. The temperature rise in the calorimeter was seldom over 1°C during an experiment. The results of his experiments give an average of 29.93 Cal. per kilogram mol. for crystalline silica, and for fused silica an average of 32.14 cal. per kilogram mol. By subtracting the heat of reaction of crystalline silica from the heat of reaction of fused silica one obtains for the value of the heat of fusion, 2.21 Cal. per kilogram mol.

The following paragraphs taken from the Journal of the Society of Glass Technology **give another method for the determination of the heat of fusion of quartz.

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*Mülert, O. Zeitschrift für Anorganische Chemie. 75, 198-240, (1912)

** M.W.Travers, Jour.Soc. of Glass Tech. IV, 220, (1920)

" The latent heat of fusion of silica is a matter of some uncertainty. Cunningham and Vogt give estimates of 0.1 K to 0.13 K per gram, based on very questionable data. Washburn has calculated the heat of fusion of cristobalite from the melting point and the composition of the eutectic Al_2O_3 SiO_2. He assumes the solute to be a simple silicate, $Al_2O_3 . SiO_2$, which separates as sillimanite at that temperature. He obtained a value of 6.8 K for the value of molal latent heat of fusion of cristobalite.

Tschernobaeff, using a calorimetric bomb determined the following heat changes from which the heat of reaction, SiO_2 crystalline → SiO_2 as glass, can be deduced. They are :

SiO_2 (sand) + Na_2CO_3 = $SiO_2 . Na_2O$ + CO_2 - 30.4K

10 SiO_2 sand + Na_2CO_3 = (9 SiO_2 Na_2SiO_3) glass + CO_2 - 96 K

If the difference -96K - 30.4 K equals the latent heat of liquefaction of 9 additional mols. of SiO_2, one obtains the value of -7.3 K which differs only slightly from the value arrived at by Washburn. One may take -7 K for the approximate value.

Tschernobaeff did not pay any attention to this pair of reactions but tried to arrive at the latent heat of SiO_2 by measuring the heat of the reaction Na_2CO_3 + 10 SiO_2 using first sand, then vitreous silica. He obtained variable results, the greatest difference corresponding to 2.3 K and the mean to 0.7 K for the molecular latent heat. It seems probable that the vitreous silica was partly devitrified."

The method used by R.Weitzel * in determining the heats of crystallization of quartz, cristobalite and chalcedony was essentially the same as that used in this investigation.

The apparatus used consisted of a Dewar flask inside of which was a platinum vessel, and inside of this a glass tube coated with paraffine. Inside of the Dewar flask three-fourths of a liter of water was placed and inside the glass coated vessel 25 cc. of hydrofluoric acid. A cork was provided to plug the opening to the platinum vessel to prevent loss of hydrofluoric acid gas. Temperatures were measured at first by means of a Beckmann thermometer and in later work with a platinum resistance thermometer. The silica was wrapped in a small paper bag and supported above the hydrofluoric acid until ready to start the experiment. This bag was torn by means of a platinum point.

In these experiments Weitzel used 0.7 grams of SiO_2 which had been ground 100 hours in an agate mortar and dried at 300°C for four hours. The reaction took on the average about 15 minutes during which time about 75 percent of the SiO_2 went into solution and gave a temperature rise of about 0.5°C.

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* Wietzel,Rudolf. Zeitschrift für Anorganische und Allgemeine chemie. 116, pg.7-95 (1921)

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The results obtained in this investigation are summarized in the following table.

	HF Used	Form of SiO_2	Heat of Sol. cal. per Mol.	Mean	Heat of Crystallization.
1	35%	quartz glass	36.01)	35.97	-
2	"	" "	35.98)		
3	"	" "	35.92)		
4	"	" crystals	33.63)	33.65	2.32
5	"	" "	33.69)		
6	"	" " ignited	33.8		2.2
7	"	cristobalite 1600°	35.37		0.60
8	"	cristobalite 1100°	35.43		0.54
9	Fuming	quartz glass	38.83		-
10	"	" crystals (not ignited)	36.48		2.35
11	"	quartz crystals (ignited)	36.65		2.2
12	"	chalcedony	36.73)	36.72	2.11
13	"	"	36.70)		
14	"	cristobalite 1100° heated at 600° in Pt.	36.55		2.28

III. EXPERIMENTAL METHOD.

It has been shown that the quantity of energy in two different forms of the same compound are different and that when these two forms are reduced to a similar compound the amount of energy liberated is different. Fused silica should contain more energy than the crystalline form. Then if the two forms were reduced to some similar compound, for example, silicon fluoride, the heat liberated in each case should be different and the difference should be the heat of fusion.

These reactions can be expressed by the following equations

$$SiO_2 \text{ (crystalline)} + 4HF \rightarrow SiF_4 + 2H_2O + H_1 \qquad (1)$$

$$SiO_2 \text{ (amorphous)} + 4HF \rightarrow SiF_4 + 2H_2O + H_2 \qquad (2)$$

subtracting equation (1) from (2)

$$H_2 - H_1 = H_3$$

These two equations do not actually express the reaction which takes place,for the SiF_4 formed reacts with the excess acid to form H_2SiF_6. The heat evolved in this reaction would cancel out in calculating the heat of fusion socould, therefore, be neglected.

The acid used in the experiments was CP 48% hydrofluoric acid. In the first set of experiments the fact that the concentration of the acid might vary with each bottle was not taken into account, but in the later determinations the required amount of acid was obtained and the contents of each bottle poured into a large glass bottle coated heavily with paraffine.

The silica was prepared by grinding in an agate mortar until it would pass through a 200 mesh screen. This method was changed in the later determinations due to the fact that only a comparatively small amount went into solution in the time allowed. The new method was to separate the heavier particles by sedimentation in water. After one-half hour the water was drawn off and the particles remaining in suspension filtered off. The fine powder obtained was heated to red heat in order to dry it completely.

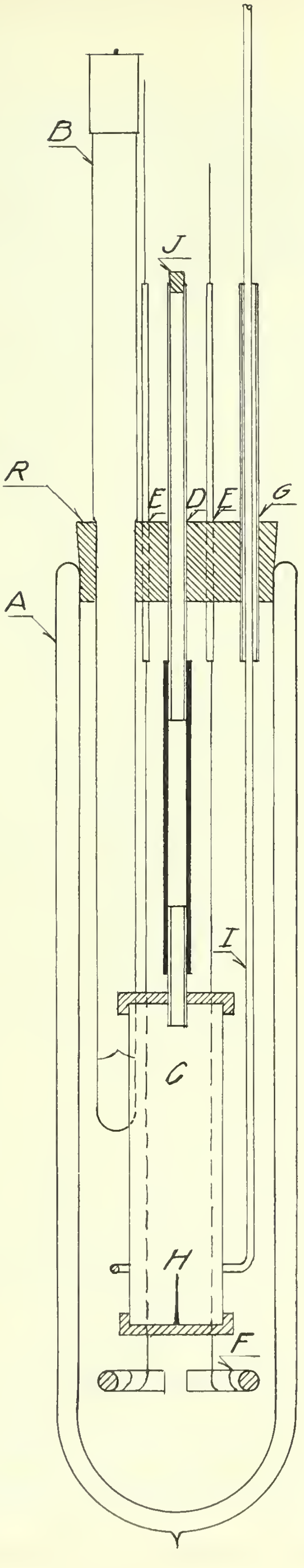
The apparatus used was changed slightly in the second set of experiments, the attempt being made to lessen the chance for error by the escape of silicon fluoride and hydrogen fluoride by stopping the opening to the copper vessel with a small rubber stopper.

A cross section of the apparatus used in the investigation is shown in Fig.7.

The calorimeter consisted of a wide mouthed Dewar flask (A) which was fitted with a rubber stopper (R). In this stopper an opening was provided for a Beckmann thermometer (B) to measure temperature rise. A glass tube (D) leading to the wax coated copper vessel (c) in which the reactions took place, was provided, two openings (E,E) for wires leading to a heating coil (F) which was used in obtaining the heat equivalent; and also an opening (G) for a stirrer.

The heating coil(F) consisted of a piece of fine constantan wire wound around a piece of glass rod bent in a circle

Fig. 1



having a diameter slightly less than the inside of the Dewar flask. The ends of the constantan wire were soldered to two copper lead wires, which passed out through the rubber stopper. The resistance of this heating coil was 3.7702 ohms.

The copper vessel (C) which contained the mixture of SiO_2 and HF during an experiment was a cylinder having an outside diameter of 35 millimeters and a height of 110 millimeters. The sides of the cylinder were made of thin sheet copper. The bottom consisted of a disc having a shoulder which slipped over the outside of the cylinder and the joint was made tight by soldering. The top consisted of a disc similar to the one on the bottom, but in this case the joint was made air tight by sealing with wax before each experiment. In the bottom of this vessel and standing about 3 cm. high was a copper wire (H) filed to a sharp point, the purpose of which was to tear open the paper bag holding the powdered silica. A small opening was provided in the top which led to the outside of the calorimeter.

The stirrer (I) consisted of a piece of glass rod bent at one end into a circle having a diameter slightly larger than the outer diameter of the copper vessel. With this type of stirrer it was possible to shake the copper vessel and stir up the mixture of acid and silica inside by twisting on the end of the stirrer, or to stir the water outside by moving the stirrer up and down along the cylinder.

The silica used in the experiment was wrapped in a small bag of thin waxed paper. This bag was held above the hydrofluoric acid, while the initial temperature was being determined,

by means of a thread which passed out through the small opening in the top. The small rubber (J) stopper provided for closing this opening and held the thread from slipping and letting the bag down in contact with the acid.

(a) Determination of the Heat Equivalent of the Calorimeter Four hundred cc. of water were placed in the Dewar flask and the copper vessel sealed with wax. The apparatus was then assembled and the calorimeter completely immersed in a thermostat. The temperature of the thermostat was regulated by adding the amount of hot water necessary to set the temperature on the outside the same as on the inside of the calorimeter. As the temperature rose during the experiment hot water was added, an attempt being made to keep the temperature within ± .05°C of the temperature inside the calorimeter. In this manner thermal leakage was reduced to a minimum. Current for heating the calorimeter was obtained from a storage battery and measured with a milliammeter. Five hundred milliamperes were allowed to flow through the coil for a certain length of time, usually one hour, time being taken accurately with a stop watch. A small adjustable resistance was placed in the circuit between the battery and milliammeter so that the current flowing could be accurately adjusted to the proper amount. Knowing the time, current, resistance of the heating element, and the temperature rise during the experiment, the heat equivalent of the calorimeter could be calculated from the formula

$$C\Delta T = \frac{I^2 R T}{4.185}$$

where C equals the heat equivalent of the calorimeter ,ΔT the temperature rise in degrees centigrade, I, the current flowing in amperes, R, the resistance of the heating element in ohms and T the time in seconds.

(b) Determination of the Heat of Fusion of Quartz.- Two grams of the finely powdered quartz were weighed accurately to 0.1 milligram and wrapped in the least possible amount of the thin waxed paper. This small sack was tied by means of a thread and suspended from the apparatus ready to assemble. Approximately 30 grams of hydrofluoric acid were poured into the copper cylinder and weighed accurately to 0.01 gram. Four hundred cc. of water were poured into the Dewar flask, the apparatus assembled and immersed in the thermostat as quickly as possible. As soon as the temperature of the thermostat had been regulated and the temperature within the calorimeter remained constant, the initial temperature was read, the small bag of quartz lowered into the hydrofluoric acid, and the cork closing the opening to the copper vessel immediately replaced. The temperature of the thermostat was regulated by adding hot water so that the temperature inside and outside would not differ by more than .05°C. At the end of one hour the final temperature was read, the mixture of hydrofluoric acid and undissolved quartz removed, and diluted by pouring into approximately 400 cc. of water. The undissolved quartz was filtered off, ignited and weighed. The amount undissolved was subtracted from the amount added to find the amount dissolved. Knowing the temperature rise during the experiment, the heat equivalent of the calorimeter and contents and the quartz dissolved, the heat

evolved per gram can be found. By repeating the experiment, using the same quantities of materials and substituting fused silica for quartz the heat evolved per gram of fused silica can be found.

IV RESULTS

In Table 1 can be found the specific heats of materials used in the investigation and not taken into account in determining the heat equivalent of the calorimeter. Although values are given for the specific heats of amorphous and fused silica, these values were not used in the later experiments. As the amount of SiO_2 used was small and changed during the experiment, the heat absorbed by it would be a variable amount and not large enough to make any considerable error if omitted entirely.

TABLE 1

Substance	Specific Heat
Hydrofluoric acid 48%	0.62
SiO_2 (Fused)	0.241 (20°C)
SiO_2 (Quartz)	0.1881 (12° - 100°C)

The Beckmann thermometer used for measuring the heat rise during a determination was standardized against a standard thermometer.

Table 2 gives the data taken in this standardization. By subtracting the corrected difference for the final temperature in an experiment from the corrected difference at the initial temperature, the correction to be added to the Beckmann reading can be found.

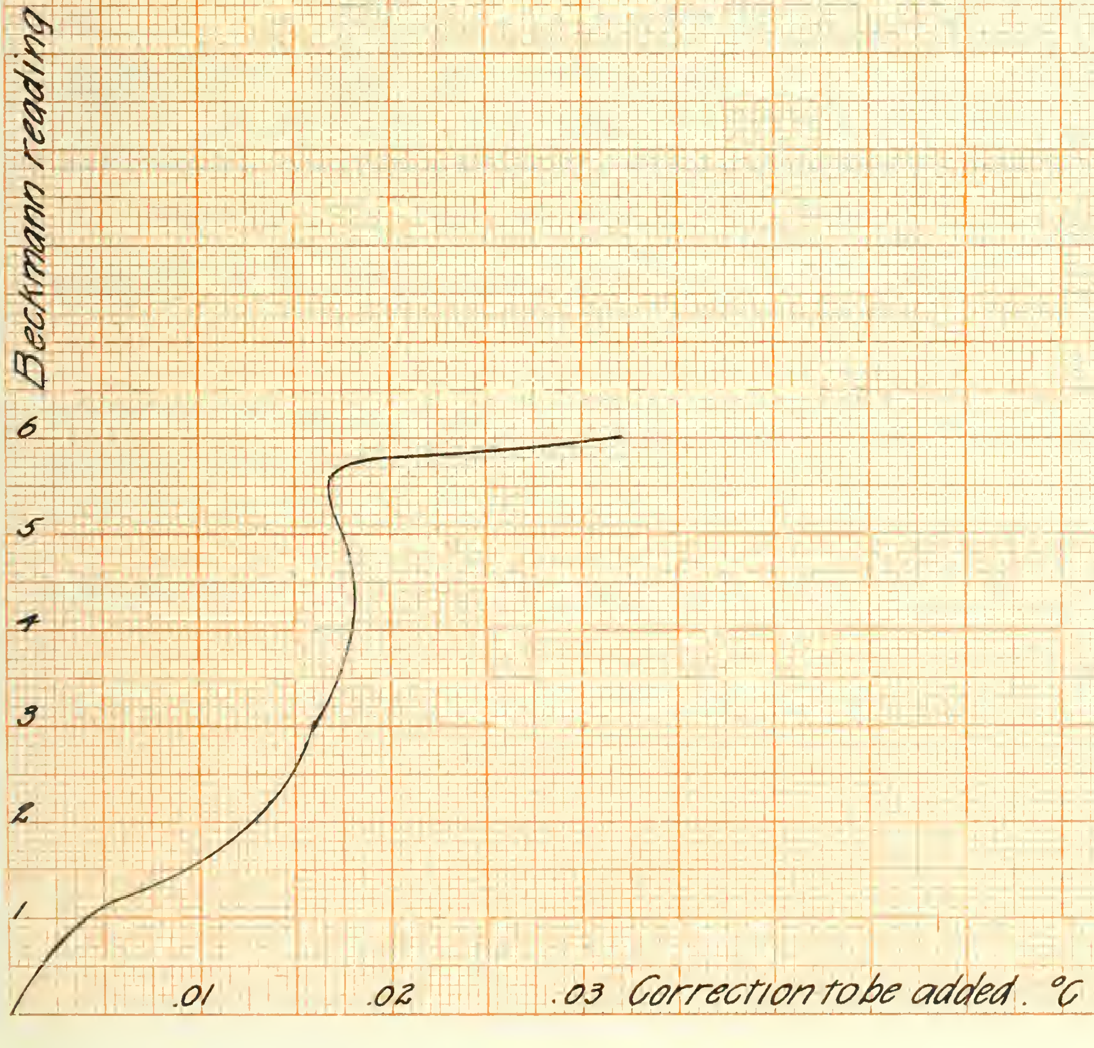
Table 2 .

Calibration of Beckmann Thermometer No.L 19

Beckmann Reading °C	Corrected Standard Reading °C	Corrected Difference	Average Difference Correction to be added.
19.911	19.134	.777	.776
19.916	19.140	.776	
21.030	20.257	.773	.772
21.030	20.259	.771	
22.103	21.340	.763	.763
22.966	22.206	.760	.760
22.955	22.194	.761	
22.930	22.173	.759	
24.058	23.300	.758	.758
24.054	23.296	.758	
25.247	24.489	.758	.7585
25.242	24.483	.759	
26.005	25.262	.743	.744
26.005	25.259	.746	
25.848	25.098	.750	.750
24.468	24.709	.759	.759

The corrections as shown in Table 2 would apply only when the Beckmann thermometer was set so that it would read 0.911 when the corrected standard reading was 19.134°C. They can, however, be made applicable to any setting of the Beckmann by taking the difference between the corrections, the difference being the corrections to be applied for any setting. These corrections have been plotted against the Beckmann reading as ordinates in Graph 1 so that it is possible to find the correction for any point on the thermometer not determined in the standardization. For example, suppose the Beckmann reading is 1.5. From the curve the value of the correction is 0.008°C, which is to be added to the thermometer reading.

Graph No. 1



The values obtained in the determination of the heat equivalent of the calorimeter are given in Tables 3 and 4, Table 3 being the ones obtained for the calorimeter used in the first set of experiments and Table 4 those for the calorimeter used in the second set.

TABLE 3.

Length of Run Minutes	Current used Milliamperes	Water added C.c.	Temp. Rise °C	Heat Equiv.	Average
25	500	350	0.853	396	
30	500	350	1.010	401.3	
45	500	350	1.524	399	398.8

Resistance of heating coil 3.7702 ohms.

TABLE 4

Length of run Minutes	Current used Milliamperes	Water added c.c.	Temp. Rise °C	Heat Equiv.	Average
30	500	400	0.898	451.5	
30	500	400	0.887	457.0	
30	500	400	0.8935	454.7	
30	500	400	0.887	457.0	
30	500	400	0.887	457.0	
30	500	400	0.885	459.2	
30	500	400	0.8785	462.0	
30	500	400	0.887	457.0	
30	500	400	0.881	460.5	457.3

Resistance of heating coil - 3.7702 ohms.

The results obtained in the experiments on the heat evolved per gram of quartz and fused silica have been placed in four tables. Two tables give the data obtained in the experiments on quartz, one for the first set of experiments, and one for the second set. The data for the experiments on fused silica have been similarly tabulated.

Table 5 gives the data obtained in the first set of experiments on quartz and the heat evolved per gram of SiO_2 as calculated from this data.

Table 5

Duration of run minutes	Weight of SiO_2 used. Grams.	Weight of HF used grams	SiO_2 dissolved grams	Temp. Rise °C	Heat Equiv. Calorimeter & contents	Heat evolved per gram of SiO_2 in cal.
60	10.0138	40.50	3.1252	3.721	430.14	512.1
64	10.0044	40.58	3.5898	4.163	431.07	501.4
60	5.0030	41.54	2.0613	2.247	431.12	469.9

Table 6 gives the data obtained using fused quartz in the first set of experiments The heat evolved per gram has been calculated from these data and also tabulated.

Table 6.

Duration of run minutes	Weight of SiO_2 used. grams	Weight of HF used. grams.	SiO_2 dissolved grams	Temp. Rise °C	Heat equiv. of calorimeter and contents	Heat evolved per gram of SiO_2. cal.
33	5.0769	40.14	4.0015	4.794	430.07	515.25
60	5.0279	40.20	3.8818	4.636	430.11	511.1
60	5.0010	40.32	3.6350	4.299	430.199	508.78
60	5.0228	40.10	3.4085	4.223	430.04	532.7
60	5.0075	40.19	3.2939	3.656	430.11	480.43
60	5.0024	45.72	3.6047	4.370	434.25	526.44
60	4.9968	40.74	3.5358	4.296	430.51	522.07
60	2.2046	42.27	1.7572	2.151	430.99	527.52

In Table 7 have been placed the data obtained in the second set of experiments on quartz. The heat evolved per gram of SiO_2 has been calculated from the data and also tabulated.

TABLE 7

Duration of run minutes	Weight of SiO_2 used. grams	Weight of HF used. grams.	SiO_2 dissolved grams	Temp. rise °C	Heat equiv. of calorimeter and contents	Heat evolved per gram of SiO_2 cal.
63	2.0000	32.15	1.1415	1.127	477.2	471.5
32	2.0007	30.75	1.2540	1.149	476.4	436.0
60	2.0000	31.15	1.5329	1.549	476.6	473.0
60	2.0000	31.28	1.5644	1.610	476.7	463.0

The data obtained in the second set of experiments for the determination of the ha heat evolved per gram of fused quartz and the values obtained by calculation from the data for the heat evolved per gram of SiO_2 have been placed in Table 8.

TABLE 8.

Duration of run minutes	Weight of SiO_2 used. grams	Weight of HF used. grams	SiO_2 dissolved grams	Temp.rise °C	Heat equiv. of calorimeter and contents	Heat evolved per gram of SiO_2 cal.
60	2.0000	30.70	1.9456	2.288	476.3	560
60	2.0000	30.79	1.9800	2.442	476.4	589
60	2.0000	30.75	1.9265	2.111	476.4	522
60	2.0000	30.2	1.8543	2.111	476.0	541.5

V. CONCLUSIONS

From the results obtained in this investigation it would be impossible to say definitely how much heat was liberated per gram of quartz when dissolved in hydrofluoric acid, and likewise for fused silica. Consequently, the heat of fusion of quartz cannot be detemined.

The reason for the unsatisfactory results is still a matter of uncertainty. Several possibilities which suggested themselves as the work progressed were tried, but all failed to give the desired results. The first reason for the discrepancies in the results, which came up while determining the heat equivalent of the calorimeter, was the possibility of errors in graduating the Beckmann thermometer. Calibrating against a standard thermometer, however, failed to show any very great errors in the Beckmann scale and the error entering from this source would easily fall within the limit of accuracy of the apparatus. At the end of the first set of experiments several other possible explanations were offered and tried in the second set, but all failed. From the values of the heats evolved per gram of quartz and fused silica in the first set of experiments it will be noticed that there ispractically no difference in the amount of heat liberated by the two forms of SiO_2. As the action of the HF on the fused SiO_2 was much faster than the action on the quartz, it was thought that the reaction $2HF + SiF_4 = H_2SiF_6$ did not go to completion due to the escape of SiF_4.

To prevent this the upper vessel containing the HF and SiO_4 was closed tightly during an experiment, but the results were still

unsatisfactory. In this case, instead of the heated evolved per gram being practically the same, the difference in the heats evolved for the two forms was too great and no checks could be obtained.

The quartz used in this investigation consisted of finely powdered sand from Ottawa, Illinois, and it was not known whether this was pure quartz crystals or a mixture of the crystals and amorphous quartz. Some of the first set of results gave approximately one half the value for the heat of fusion as obtained by others and it was thought that this quartz might consist of a mixture of the two forms in about equal parts. The second series of experiments indicated, however, that this was not the case.

Finer silica prepared by sedimentation, was used in the second set of experiments for the purpose of obtaining a larger heat rise, the finer silica being attacked by the acid more readily and more being dissolved. The larger heat rise would lessen the effect of any errors in reading the thermometer. In the first four experiments this silica was dried at 200°C for 24 hours and the failure to give results was thought to be due to the presence of considerable water held by the finely powdered silica. It was then dried for about an hour at 800°C, but the following experiments gave no better results.

Whether the fault lies with the apparatus or the materials used is doubtful, but from all indications the whole trouble seems to lie with the materials, for results which checked within the limits of accuracy of the apparatus were easily obtained in the determination of the heat equivalent of the calorimeter. The

quartz and fused silica were both found to contain considerable iron which probably came from the distilled water during the preparation of the silica by sedimentation. The fused silica appeared to contain the most iron, but whether this would be responsible for the error was not determined.

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